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(54) Title: BREATHABLE FILMS

(57) Abstract: One aspect of the present invention concerns a composition for preparing breathable films. The composition comprises a bimodal polyethylene composition, a particulate filler, and optionally, an olefin-based polymer. The bimodal polyethylene composition has a melt flow rate MFR₂ of 0.1 to 4 g/10 min and a density of 918 to 935 kg/m³. The olefin-based polymer can be, e.g., polypropylene. The films prepared from the composition have a very high water vapour transmission rate, exceeding 3000 g/m²/24 h. The composition can be prepared to thin films having a low basis weight, of 25 g/m² or less. The films have no pinholes.

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BREATHABLE FILMS

Background of the Invention

5 **Field of the Invention**

The present invention concerns breathable films prepared from linear low-density polyethylene compositions. In addition, the present invention concerns bimodal linear low-density polyethylene compositions used for preparing breathable films. In particular, the
10 present invention relates to breathable films having an improved mechanical strength.

Description of Related Art

It is known in the art to prepare breathable films by blending thermoplastic polymers with
15 fillers and stretching the films so, that voids are formed adjacent to the filler particles.

WO-A-01/79343 discloses a microporous thermoplastic film having an improved impact strength and high moisture vapour transmission rate. The film is prepared from a blend containing 40 to 60 % calcium carbonate, 30 to 40 % linear low density PE and 1 to 10 %
20 low density PE. The film is then incrementally stretched to provide the microporous film.

WO-A-99/32164 discloses an absorbent article with a topsheet, backsheet and an absorbent layer between the two. The backsheet comprises a microporous polymer film containing 30 to 60 % polyolefin and 40 to 80 % calcium carbonate. After the film is cast, it is drawn to
25 form the microporous holes around the calcium carbonate filler. Polyethylene was used in the example.

WO-A-99/14262 discloses a breathable film made of a composition containing a first ethylene polymer, having a density lower than 890 kg/m³, a second ethylene polymer
30 having a density above 900 kg/m³ and at least 35 % of a filler. The ratio between the first ethylene polymer and the second ethylene polymer is 25/75 – 75/25. The film was stretched to make it porous. The examples showed that metallocene based PE was used both as the first ethylene polymer and the second ethylene polymer.

While the above documents disclose different breathable films and compositions for preparing them, there still remains a need for films having a high water vapour transmission rate combined with good mechanical properties and good processability.

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Summary of the Invention

It is an object of the present invention to provide breathable films having good mechanical properties and good processability.

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These and other objects, together with the advantages thereof over known processes and products, which shall become apparent from the specification, which follows, are accomplished by the invention as hereinafter described and claimed.

15 The present invention is based on the provision of compositions comprising:

(i) 20 – 50 %, based on the weight of the total composition, a bimodal polyethylene composition comprising

20 (i-a) a first (low molecular weight) component with a melt flow rate MFR_2 of 50 to 500 g/10 min, preferably of 100 to 400 g/10 min and a density of 940 to 975 kg/m³, preferably 945 to 975 kg/m³, the first component being present in the bimodal polyethylene composition in an amount of 37 to 48 % by weight,

25 (i-b) at least one other component having a higher molecular weight (or a lower melt flow rate) and a lower density than the said first component, the second component being present in the bimodal polyethylene composition in an amount of 52 to 63 % by weight, so that the said bimodal polyethylene composition has a melt flow rate MFR_2 in the range of 0.1 to 4.0 g/10 min, preferably 0.1 to 0.8 g/10 min, MFR_{21} in the range of 15 to 200 g/10 min, preferably 15 to 70 g/10 min and a density of 918 to 935 kg/m³,

(ii) 40 – 70 %, based on the weight of the total composition, a particulate filler, and

30 (iii) 0 – 30 %, based on the weight of the total composition, another olefin-based polymer.

Additionally, the present invention provides a process for producing the polymer composition. First, the said bimodal polyethylene composition is produced in situ by

polymerising or copolymerising ethylene in a reactor cascade formed by at least a first reactor and a second reactor in the presence of a polymerisation catalyst. The polymerisation catalyst has been prepared by supporting a magnesium compound, an aluminium compound and a titanium compound on a particulate support. Second, the
5 bimodal composition is blended with the particulate filler and optionally, the other olefin based polymer.

One more aspect of the present invention is to provide breathable, microporous films having improved properties.

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A further aspect of the invention is to provide the use of the above-mentioned composition for breathable films.

15

Still one more aspect of the invention is to provide a process for preparing breathable films.

Next, the invention will be more closely examined with the aid of the following detailed description and examples.

20 **Detailed Description of the Invention**

Definitions

For the purpose of the present invention, "slurry reactor" designates any reactor operating
25 in slurry, in which reactor the polymer forms in particulate form. As examples of suitable reactors can be mentioned a continuous stirred tank reactor, a batch-wise operating stirred tank reactor or a loop reactor. According to a preferred embodiment the slurry reactor comprises a loop reactor.

30 By "gas phase reactor" is meant any mechanically mixed or fluidised bed reactor. Preferably the gas phase reactor comprises a fluidised bed reactor with gas velocities of at least 0.2 m/sec, which may further have a mechanical agitation.

By "melt flow rate" or abbreviated "MFR" is meant the weight of a polymer extruded through a standard cylindrical die at a standard temperature (190 °C for polyethylene) in a laboratory rheometer carrying a standard piston and load. MFR is a measure of the melt viscosity of a polymer and hence also of its molecular weight. The abbreviation "MFR" is generally provided with a numerical subscript indicating the load of the piston in the test. Thus, e.g., MFR₂ designates a 2.16 kg load. MFR can be determined using, e.g., by one of the following tests: ISO 1133 C4, ASTM D 1238 and DIN 53735.

The composition

One aspect of the present invention provides a composition for making breathable films having a high rate of water vapour transmission (WVTR), the composition comprising:

(i) 20 – 50 %, based on the weight of the total composition, a bimodal polyethylene composition comprising

(i-a) a first (low molecular weight) component with a melt flow rate MFR₂ of 50 to 500 g/10 min, preferably of 100 to 400 g/10 min and a density of 940 to 975 kg/m³, preferably 945 to 975 kg/m³, the first component being present in the bimodal polyethylene composition in an amount of 37 to 48 % by weight,

(i-b) at least one other component having a higher molecular weight (or a lower melt flow rate) and a lower density than the said first component, the second component being present in the bimodal polyethylene composition in an amount of 52 to 63 % by weight, so that the said bimodal polyethylene composition has a melt flow rate MFR₂ in the range of 0.1 to 4.0 g/10 min, preferably 0.1 to 0.8 g/10 min, MFR₂₁ in the range of 15 to 200 g/10 min, preferably 15 to 70 g/10 min and a density of 918 to

935 kg/m³,

(ii) 40 – 70 %, based on the weight of the total composition, a particulate filler, and

(iii) 0 – 30 %, based on the weight of the total composition, another olefin-based polymer.

Bimodal polyethylene composition

The use of bimodal polyethylene component gives the compositions of the present invention a high mechanical strength. It also gives the compositions a good processability and allows the preparation of thin films having a low basis weight. Very high water vapour transmission rates can be reached, with no pinholes in the film.

As referred to above, the bimodal polyethylene composition comprises 20 – 50 % of the composition, based on the total weight of the composition. The bimodal polyethylene composition preferably further comprises of 37 – 48 % of a low molecular weight component and 52 – 63 % of a high molecular weight component, based on the weight of the bimodal polyethylene composition.

The low molecular weight component helps to improve the processability of the composition. It preferably has an MFR_2 of about 50 to 500 g/10 min, more preferably 100 to 400 g/10 min. It may be a copolymer of ethylene with a $C_4 - C_{10}$ alpha-olefin comonomer so that it has a density of about 940 kg/m^3 or higher, preferably of about 945 kg/m^3 or higher, but it may also be a homopolymer of ethylene having a density of higher than about 970 kg/m^3 , and in particular of about 975 kg/m^3 .

The high molecular weight component gives the mechanical properties to the composition. It is a copolymer of ethylene with a $C_4 - C_{10}$ alpha-olefin, and it has a higher molecular weight and a higher content of comonomer than the low molecular weight component. It has such molecular weight and comonomer content that at given properties of the low molecular weight component and at a given split of the components, the bimodal polyethylene composition has the desired melt index and density.

According to one preferred embodiment of the invention, the low molecular weight component is a copolymer of ethylene and a $C_4 - C_{10}$ alpha-olefin, having a melt flow rate MFR_2 of 50 to 500 g/10 min, preferably of 100 to 400 g/10 min and a density of 940 to 955 kg/m^3 , preferably 945 to 953 kg/m^3 . The bimodal polyethylene composition has a melt flow rate MFR_2 of 0.4 to 0.8 g/10 min, and a density of 918 to 925 kg/m^3 .

According to another preferred embodiment of the invention, the low molecular weight component is a copolymer of ethylene and a $C_4 - C_{10}$ alpha-olefin, having a melt flow rate MFR_2 of 100 to 500 g/10 min, preferably of 200 to 400 g/10 min and a density of 940 to 955 kg/m^3 , preferably 945 to 953 kg/m^3 . The bimodal polyethylene composition has a melt flow rate MFR_2 of 0.1 to 0.3 g/10 min, MFR_{21} of 15 to 35 g/10 min and a density of 918 to 925 kg/m^3 .

According to still another preferred embodiment of the invention, the low molecular weight component is a homopolymer of ethylene having a melt flow rate MFR_2 of 100 to 500 g/10 min, preferably of 200 to 400 g/10 min and a density of higher than about 970 kg/m³. The bimodal polyethylene composition has a melt flow rate MFR_2 of 0.1 to 0.3 g/10 min, MFR_{21} of 15 to 35 g/10 min and a density of 925 to 935 kg/m³.

As seen from another aspect of the invention, the bimodal polyethylene composition has a density between about 912 and 935 kg/m³, preferably between about 918 and 935 kg/m³, a melt flow rate MFR_2 of from about 0.05 to 4.0 g/10 min, preferably from about 0.1 to 0.8 g/10 min, a melt flow rate MFR_{21} of from about 7 to 200 g/10 min, preferably from about 15 to 70 g/10 min and a flow rate ratio $FRR_{21/2}$, defined as the ratio of MFR_{21} to MFR_2 of from about 40 to 180, preferably from about 60 to 120.

Preferably, the bimodal polyethylene composition further has a weight average molecular weight M_w of from about 90000 to 320000 g/mol, more preferably from 150000 to 300000 g/mol, a molecular weight distribution defined as the ratio of the weight average molecular weight M_w to the number average molecular weight M_n of from 5 to 40, more preferably from 7 to 30. Preferably still, the bimodal polyethylene composition has a content of alpha-olefin comonomer units in the polymer chain of about 2 to 5 mol-%, more preferably 2.5 to 4 mol-%.

Particulate filler

The particulate filler is a solid material in the form of particles, which can be uniformly dispersed over the film. Advantageously, the particulate filler has an average particle size within the range of 0.1 to 10 μ m, preferably 0.1 to 4 μ m. Examples of such fillers are calcium carbonate, magnesium carbonate, barium carbonate, sodium carbonate, different clays, silica, alumina, barium sulphate, diatomaceous earth, magnesium sulphate, mica, carbon, calcium oxide, magnesium oxide etc. The filler particles may also be coated with a fatty acid to improve the flow properties of the particles. Calcium carbonate is especially preferred particulate filler.

The particulate filler comprises 40 – 70 % of the total weight of the composition. It is the present understanding that when the composition is extruded to a film and the film is stretched, micropores are formed adjacent to the filler particles. These micropores allow

the passage of gases and vapours through the film. On the other hand, the micropores are small enough to prevent the passage of liquids through the film.

Olefin-based polymer

5 The olefin-based polymer, which may be present in the compositions of the present invention, may be a homo- or copolymer of ethylene, propylene, 1-butene, 4-methyl-1-pentene etc, which is different from the bimodal polyethylene composition referred to above. Preferably, the olefin-based polymer is incompatible with the bimodal polyethylene composition. Thus, it has been found that high-impact propylene copolymers are suitable
10 to be used in the present invention. Additional preferred polymers, which may be used as the olefin-based polymer, are other propylene homo- or copolymers, 1-butene homo- or copolymers and 4-methyl-1-pentene homo- or copolymers.

Process for making the composition

15

Polymerisation catalyst

The polymerisation catalyst preferably contains a magnesium compound, an aluminium compound and a titanium compound supported on a particulate support. Also, a catalyst comprising titanium compound supported on solid magnesium halide particles may be
20 used.

If a catalyst supported on a particulate support is used, then the particulate support can be an inorganic oxide support, such as silica, alumina, titania, silica-alumina and silica-titania. Preferably, the support is silica.

25

The average particle size of the silica support can be typically from 10 to 100 μm . However, it has turned out that special advantages can be obtained if the support has an average particle size from 15 to 30 μm , preferably from 18 to 25 μm . Especially it has been found out that the average particle size of the polymer produced in the process of the
30 invention is the same irrespective whether the catalyst is prepared on a 20 μm support or on a 40 μm support. In fact, the fraction of fine polymer particles has been found to be lower if a support having an average particle size of 20 μm is used. The reduction of the fine polymer reduces the risk of plugging and thus contributes to a stable process

operation. This, on the other hand, helps to produce polymer films with a good homogeneity.

The magnesium compound is a reaction product of a magnesium dialkyl and an alcohol.

5 The alcohol is a linear or branched aliphatic monoalcohol. Preferably, the alcohol has from 6 to 16 carbon atoms. Branched alcohols are especially preferred. 2-ethyl-1-hexanol is one example of the preferred alcohols. The magnesium dialkyl may be any compound of magnesium bonding to two alkyl groups, which may be the same or different. Butyl-octyl magnesium is one example of the preferred magnesium dialkyls.

10

The aluminium compound is chlorine containing aluminium alkyl. Especially preferred compounds are aluminium alkyl dichlorides and aluminium alkyl sesquichlorides.

15 The titanium compound is a halogen containing titanium compound, preferably chlorine containing titanium compound. Especially preferred titanium compound is titanium tetrachloride.

20 The catalyst can be prepared by sequentially contacting the carrier with the above mentioned compounds, as described in EP-A-688794. Alternatively, it can be prepared by first preparing a solution from the components and then contacting the solution with a carrier, as described in WO-A-01/55230.

25 The above mentioned solid catalyst component is contacted with a aluminium alkyl cocatalyst, which preferably is an aluminium trialkyl compound, after which it can be used in polymerisation. The contacting of the solid catalyst component and the aluminium alkyl cocatalyst can either be conducted prior to introducing the catalyst into the polymerisation reactor, or it can be conducted by introducing the two components separately into the polymerisation reactor.

Polymerisation process

To produce the polymer compositions according to the invention, ethylene is polymerised in the presence of a polymerisation catalyst at elevated temperature and pressure. Polymerisation is carried out in a series of polymerisation reactors selected from the group
5 of slurry and gas phase reactors. In the most preferred embodiment, the reactor system comprises one loop reactor (referred to in the subsequent text as "the first reactor") and one gas phase reactor (referred to in the subsequent text as "the second reactor"), in that order.

However, it should be understood that the reactor system can comprise other reactors in
10 addition to the first and the second reactor. Thus, it is possible to include reactors, e.g. for prepolymerisation, or to divide either one of the reactors in two or more reactors.

The high molecular weight portion and the low molecular weight portion of the product can be prepared in any order in the reactors. A separation stage is normally needed
15 between the reactors to prevent the carryover of reactants from the first polymerisation stage into the second one. The first stage is typically carried out using an inert reaction medium.

The catalyst used in the polymerisation process can be a Ziegler-Natta or a metallocene
20 catalyst. According to a preferred embodiment, a Ziegler-Natta catalyst is used. According to another preferred embodiment, no fresh catalyst is added to the second polymerisation stage.

In every polymerisation step it is possible to use also comonomers selected from the group
25 of C₃₋₁₈ olefins, preferably C₄₋₁₀ olefins, such as 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene and 1-decene as well as mixtures thereof.

In addition to the actual polymerisation reactors used for producing the bimodal ethylene homo- or copolymer, the polymerisation reaction system can also include a number of
30 additional reactors, such as prereactors. The prereactors include any reactor for prepolymerising the catalyst and for modifying the olefinic feed, if necessary. All reactors of the reactor system are preferably arranged in series (in a cascade).

According to a preferred embodiment of the invention, the polymerisation comprises the steps of:

- (i) 5 subjecting ethylene, hydrogen and optionally comonomer(s) to a first polymerisation or copolymerisation reaction in the presence of the polymerisation catalyst in a first reaction zone in a loop reactor to produce a first reaction product having a low molecular weight with a melt flow rate MFR_2 of 50 to 500 g/10 min, preferably of 100 to 400 g/10 min and a density of 940 to 975 kg/m³, preferably 945 to 975 kg/m³,
- (ii) recovering the first polymerisation product from the first reaction zone,
- 10 (iii) feeding the first polymerisation product to a second reaction zone or reactor,
- (iv) feeding additional ethylene, comonomers and optionally hydrogen to the second reaction zone,
- (v) subjecting the additional ethylene and additional comonomer(s) and optionally hydrogen to a second polymerisation reaction in the presence of the said polymerisation catalyst and the first polymerisation product,
- 15 (vi) to produce a polymer composition comprising from 41 to 48 % by weight of the low molecular weight polymer produced in step (i), and from 59 to 52 % by weight of the high molecular weight component produced in step (v),
- (vii) the composition having a melt flow rate in the range MFR_2 of 0.1 to 4.0 g/10 min, preferably 0.1 to 0.8 g/10 min and a density of 918 to 935 kg/m³, and
- 20 (viii) recovering the combined polymerisation product from the second reaction zone.

In the first step of the process, ethylene with the comonomer(s) is fed into the first polymerisation reactor. Along with these components is fed also hydrogen, which
25 functions as a molecular weight regulator. The amount of hydrogen depends on the desired molecular weight of the polymer. The catalyst may be fed to the reactor together with the reagents or, preferably, in a separate stream, normally by flushing with a diluent.

The polymerisation medium typically comprises the monomer (i.e. ethylene) and/or a
30 hydrocarbon, in particular, a light inert hydrocarbon, such as propane, isobutane, n-butane or isopentane. The fluid is in liquid, gaseous or supercritical state. In the supercritical state the temperature and the pressure of the reaction mixture exceed the critical temperature and critical pressure of the fluid mixture. In the case of a loop reactor, the fluid is either in liquid or supercritical state and the suspension of polymer is circulated continuously

through the slurry reactor, whereby a suspension of polymer in particle form in a hydrocarbon medium or monomer will be produced.

5 The conditions of the loop reactor are selected so that 37 – 48 wt-%, preferably 39 – 47 wt-%, of the whole production is polymerised in the loop reactor(s). The temperature is in the range of 40 to 110 °C, preferably in the range of 70 to 100 °C. The reaction pressure is in the range of 25 to 100 bar, preferably 35 to 80 bar. The mole fraction of ethylene in the reaction mixture is typically of 4 to 10 %, preferably of 5 to 9 %. The ratio of the alpha-olefin comonomer to ethylene depends on the density of the polymer that is produced in
10 the first stage; typically it is of 0 to 800 mol/kmol.

Hydrogen is also fed into the first reactor to control the molecular weight (or melt flow rate) of the polymer. The exact ratio of hydrogen to ethylene depends on the desired melt flow rate of the polymer to be produced; typically it is of 100 to 600 mol/kmol, preferably
15 of 150 to 400 mol/kmol.

The polymerisation heat is removed by cooling the reactor with a cooling jacket. The residence time in the slurry reactor must be at least 10 minutes, preferably 40-80 min for obtaining a sufficient degree of polymerisation.
20

After the first reaction zone at least part of the volatile components of the reaction medium are evaporated. As a result of the evaporation, at least the major part of hydrogen is removed from the product stream. The product stream is then subjected to a second polymerisation stage in the gas phase reactor in the presence of additional ethylene to
25 produce a high molecular weight polymer.

The second reactor is a gas phase reactor, wherein ethylene, comonomers and preferably hydrogen are polymerised in a gaseous reaction medium in the presence of the polymerisation catalyst.
30

The gas phase reactor can be an ordinary fluidised bed reactor, although other types of gas phase reactors can be used. In a fluidised bed reactor, the bed consists of the formed and growing polymer particles as well as still active catalyst that enters the reactor with the polymer stream. The bed is kept in a fluidised state by introducing gaseous components,

for instance monomer and comonomer(s) from the bottom of the reactor on such a flow rate that the particles are supported but not entrained by the gas stream. The fluidising gas can contain also inert gases, like nitrogen and propane and also hydrogen as a molecular weight modifier. The fluidised bed gas phase reactor can be equipped with a mechanical mixer.

The gas phase reactor used can be operated in the temperature range of 50 to 115 °C, preferably between 60 and 100 °C and the reaction pressure between 10 and 40 bar and the partial pressure of ethylene between 2 and 20 bar, preferably between 3 and 8 bar.

The production split between the low molecular weight polymerisation reactor and the high molecular weight polymerisation reactor is (37 to 48 %): (63 to 52 %), based on the weight of the polymer composition. Preferably, 39 to 47 wt- of the ethylene copolymer is produced at conditions to provide a polymer having an MFR₂ of 50 to 500 g/10 min, preferably of 100 to 400 g/10 min and a density 940 to 975 kg/m³, preferably 945 to 975 kg/m³. Respectively, it is preferred that 53 to 61 % of the ethylene copolymer is produced at conditions to provide the high molecular weight polymer, having been produced in such conditions that the final polymer composition has an MFR₂ of 0.1 to 4.0 g/10 min, preferably 0.1 to 0.8 g/10 min, and a density of 918 to 925 kg/m³.

As mentioned above, the ratio of comonomer to ethylene in the second reactor is selected so that the final polymer composition has the desired density. A suitable range is 500 to 900 mol/kmol, preferably 500 to 800 mol/kmol.

In a similar fashion, the ratio of hydrogen to ethylene in the second reactor is selected so that the final polymer composition has the desired melt flow rate. A typical range is 1 to 30 mol/kmol, preferably 3 to 20 mol/kmol.

The present polymers and copolymers of ethylene can be blended and optionally compounded with additives and adjuvants conventionally used in the art. Thus, suitable additives include antistatic agents, flame retardants, light and heat stabilisers, pigments and processing aids.

Compounding

After the polymer is collected from the reactor and the hydrocarbon residues are removed therefrom, the polymer is compounded and extruded to pellets. In this process step, any extruder known in the art may be used. It is preferred, however, to use a twin screw
5 extruder. It may be of a co-rotating type, such as those produced by Werner & Pfleiderer having a designation ZSK, e.g. ZSK 90 having a 90 mm screw diameter. Alternatively, it may be of a counter-rotating type, such as those produced by Japan Steel Works, having a designation JSW CIM-P, e.g. CIM90P, having a 90 mm screw diameter. It is especially preferred to use a counter-rotating twin screw extruder.

10

The particulate filler and optionally, the olefin-based polymer may be added to the bimodal polyethylene composition at this extrusion stage. It is possible, however, to mix the bimodal polyethylene composition with additives, and extrude it to pellets. These pellets are then introduced into a second extrusion stage, to which also the particulate filler and
15 optionally, the olefin-based polymer, is introduced. The thus obtained compound may then be extruded directly into a film. However, it may also be extruded to pellets, which are collected and extruded to a film in a separate extrusion stage.

Films

20

The composition according to the present invention is used to prepare breathable films. The films may be produced either by blowing or casting. The polymers having a melt index at the lower end of the MFR range, having MFR₂ of 0.1 to 0.8 g/10 min, are suitable for film blowing. On the other hand, the polymers having a melt index at the higher end of
25 the MFR range, having MFR₂ of 0.4 to 4.0 g/10 min, are suitable for making cast films.

After the film has been prepared, it shall be stretched. The purpose of stretching is to produce micropores adjacent to the filler particles, thus making the film breathable. The film shall be stretched from 3 to 10 times, preferably 4 to 7 times, its original length. This
30 ratio between the length of the stretched film and the length of the original film is in the subsequent text referred to as the stretching ratio.

Surprisingly, the films of the present invention have a very high water vapour transmission rate. To achieve this high rate, it is advantageous to use a high fraction of filler particles

(from 57 to 70 %) in the composition, preferably together with a high stretching ratio (from 5.5 to 7).

5 It appears that the high mechanical strength and the good processability of the bimodal polyethylene composition make it possible to use high stretching ratios. This allows to reach a very high water vapour transmission rate, higher than $3000 \text{ g/m}^2/24 \text{ h}$, in fact even higher than $4000 \text{ g/m}^2/24 \text{ h}$.

10 Alternatively and surprisingly, water vapour transmission rate higher than $3000 \text{ g/m}^2/24 \text{ h}$, or even higher than $4000 \text{ g/m}^2/24 \text{ h}$ can be obtained by providing a composition comprising 25 to 40 % of the bimodal polyethylene composition, 50 to 57 % of the particulate filler and 5 to 20 % of a propylene polymer. When this composition is prepared into a film and stretched with a stretching ratio of 4 to 5.5, the resulting film has the high water vapour transmission rate referred to above.

15

The effect of the presence of the propylene polymer on the water vapour transmission rate is surprisingly strong. It was found that the rate could be increased by more than 100 % by adding the propylene polymer into the composition, compared to a similar composition where the propylene polymer was not present. The propylene polymers that can be used to
20 increase the water vapour transmission rate include, propylene homopolymers, random copolymers of propylene with other olefins, especially ethylene, high impact propylene copolymers and propylene-ethylene rubbers. It is believed that polymers of other olefins, which are not miscible with the bimodal polyethylene, such as homo- and copolymers of 1-butene or 4-methyl-1-pentene would have a similar effect.

25

Also, thin films having a low basis weight can be obtained without pinholes. Thus, the films of the present invention have can have a thickness of $25 \mu\text{m}$ or less, even $20 \mu\text{m}$ or less, and they can have a basis weight of 25 g/m^2 or less, even 20 g/m^2 or less. This makes it possible to prepare the films from a smaller amount of polymer, thus allowing to save in
30 raw material costs.

One more surprising advantage of the use of the bimodal polyethylene composition as a base polymer in the composition is the reduction of the amount of scrap material when producing the films and the compositions, compared with the situation when a unimodal

polyethylene is used as a base polymer in the composition. It appears that the use of the bimodal polyethylene composition gives a good homogeneity of the composition, and therefore the amount of waste is substantially reduced. This improves the economy of the film preparation process.

5

The films according to the present invention have a high mechanical strength. Thus, they have a higher tensile strength and tear strength than the prior art films made from a unimodal polyethylene composition. Preferably, the films according to the present invention have a tensile strength in the machine direction of at least 30 MPa, more preferably at least 40 MPa, a tensile strength in the transverse direction of at least 2 MPa, more preferably at least 3 MPa, a tear strength in the machine direction of at least 0.5 N, more preferably 0.8 N and in the transverse direction of at least 20 N, more preferably at least 30 N.

15 Description of Analytical Methods

Tensile strength

The experiment is performed according to ISO 1184 method. The specimen is extended along its major axis at a constant speed. Normal 50 mm could be used as a distance between grips (gauge length) in film tensile testing. 125 mm gauge length is required for tensile modulus measurement.

Tear strength

Tear testing is done according to ASTM 1922.

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Water vapour transmission rate (WVTR)

Water vapour transmission rate was measured by using Permatran – W 100K water vapour permeation analysis system, commercially available from Modern Controls, Inc. (MOCON).

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Basis weight

Basis weight can be determined in accordance with Federal Test Method No. 191A/5041. Sample size for the sample materials was 15.24×15.24 cm, and the resulting value is an average of at least three individual measurements.

Pinholes number

The presence of pinholes is determined by subjecting a film sample to water pressure corresponding to 650 mm water height.

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Density

Density was determined from compression moulded specimen at 23 °C in a water bath according to an ultrasound measurement method using Tecrad DS 500 equipment. The method was calibrated with samples having a density determined according to ISO 1183.

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Molecular weight

Molecular weight distribution and average molecular weights were determined by size exclusion chromatography (SEC). In the examples a Waters 150 CV plus No. 1115 instrument was used, with a refractive index (RI) and viscosity detector. The columns were 15 3 HT6E styragel from Waters. The oven temperature was 140 °C. The instrument was calibrated by using a polystyrene sample having a narrow molecular weight distribution.

Comonomer content

The comonomer content is determined by using ^{13}C NMR.

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Melt flow rate

The melt flow rate of the polymer was determined according to ISO 1133 at 190 °C. The load was indicated as a subscript, e.g. MFR₂₁ was determined under 21.6 kg load.

25 Average particle size

The average particle size was determined by sieving the polymer.

For catalyst and filler the average particle size is determined as a volume average particle size, using, e.g. Coulter LS Particle Size Analyser.

30 The invention is further illustrated with the aid of the following examples.

Example 1 (Preparation of the catalyst)Complex preparation:

87 kg of toluene was added into the reactor. Then 45.5 kg Bomag A in heptane was also added in the reactor. 161 kg 99.8 % 2-ethyl-1-hexanol was then introduced into the reactor at a flow rate of 24-40 kg/h. The molar ratio between BOMAG-A and 2-ethyl-1-hexanol was 1:1.83.

Solid catalyst component preparation:

275 kg silica (ES747JR of Crossfield, having average particle size of 20 μm) activated at 600 °C in nitrogen was charged into a catalyst preparation reactor. Then, 411 kg 20 % EADC (2.0 mmol/g silica) diluted in 555 litres pentane was added into the reactor at ambient temperature during one hour. The temperature was then increased to 35 °C while stirring the treated silica for one hour. The silica was dried at 50 °C for 8.5 hours. Then 655 kg of the complex prepared as described above (2 mmol Mg/g silica) was added at 23 °C during ten minutes. 86 kg pentane was added into the reactor at 22 °C during ten minutes. The slurry was stirred for 8 hours at 50 °C. Finally, 52 kg TiCl_4 was added during 0.5 hours at 45 °C. The slurry was stirred at 40 °C for five hours. The catalyst was then dried by purging with nitrogen.

Example 2 (Preparation of the bimodal composition)

Into a 500 dm^3 loop reactor, operated at 85 °C temperature and 60 bar pressure, was continuously introduced propane diluent, ethylene, hydrogen and 1-butene comonomer in such flow rates that ethylene content in the reaction mixture was 6.7 mol-%, the mole ratio of hydrogen to ethylene was 235 mol/kmol and the mole ratio of 1-butene to ethylene was 570 mol/kmol. At the same time into the reactor was continuously introduced a polymerisation catalyst prepared according to Example 1 and triethylaluminium cocatalyst in such quantities that ethylene polymer was produced at a rate of 25 kg/h. The molar ratio of aluminium of the cocatalyst to titanium of the catalyst was 20. The polymer had an MFR_2 of 300 g/10 min and density of 951 kg/m^3 .

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The polymer was withdrawn from the loop reactor by using settling legs, and the polymer slurry was introduced into a flash tank operated at 3 bar pressure and 20 °C temperature.

From the flash tank the polymer was introduced into a fluidised bed gas phase reactor, which was operated at 80 °C temperature and 20 bar pressure. Into the gas phase reactor were additional ethylene, hydrogen and 1-butene introduced, as well as nitrogen flushes to keep the connections and piping open. Consequently, the concentration of ethylene in the reactor gas was 19 mol-%, the molar ratio of hydrogen to ethylene was 3 mol/kmol and the molar ratio of 1-butene to ethylene was 645 mol/kmol. The polymer was withdrawn from the reactor at a rate of 56 kg/h. After collecting the polymer, it was blended with additives and extruded into pellets in a counterrotating twin-screw extruder JSW CIM90P. The resulting polymer had an MFR₂ of 0.47 g/10 min and density of 922 kg/m³. The split, defined as a weight ratio of the polymer produced in the loop reactor to the polymer produced in the gas phase reactor, was 45/55.

Example 3

The procedure of Example 2 was repeated, except that the conditions in the reactors were changed. The conditions and the resulting polymer data can be found in Table 1.

Example 4

The procedure of Example 2 was repeated, except that the conditions in the reactors were changed. The conditions and the resulting polymer data can be found in Table 1.

Example 5

Polymer produced in Example 4 was compounded with SA233F (a high-impact copolymer of propylene with ethylene, produced and marketed by Borealis, having ethylene content of 14.5 % by weight and MFR₂, determined at 230 °C, of 0.8 g/10 min) and calcium carbonate. The final composition contained 35 % by weight of the bimodal polyethylene composition of Example 4, 10 % by weight of SA233F and 55 % by weight of CaCO₃. The thus obtained composition was then blown to a film and the resulting film was stretched in the machine direction 4.7 times its original length. The resulting film had a thickness of 30 µm, a basis weight of 34 g/m², tensile strength in the machine direction of 50 MPa, and in the transverse direction of 5 MPa. Tear strength in the machine and transverse directions were 1.2 and 40 N, respectively. The water vapour transmission rate was found to be 4990 g/m²/24 h. The film had no pinholes.

Table 1: Production data of Examples 2,3 and 3

Example	2	3	4
Ethylene concentration in loop reactor, mol-%	6.7	6.7	6.7
Hydrogen to ethylene ratio in loop reactor, mol/kmol	235	265	305
1-butene to ethylene mole ratio in loop reactor, mol/kmol	570	514	0
Polymer production rate in loop reactor, kg/h	25	26	25
MFR ₂ of polymer produced in loop reactor, g/10 min	300	580	300
Density of polymer produced in loop reactor, kg/m ³	951	951	975
Ethylene concentration in gas phase reactor, mol-%	19	7.8	8.2
Hydrogen to ethylene ratio in gas phase reactor, mol/kmol	3	7	8
1-butene to ethylene mole ratio in gas phase reactor, mol/kmol	645	460	480
Average particle size of the powder, mm	0.38	0.36	ND
MFR ₂ of the final polymer, g/10 min	0.47	0.21	ND
MFR ₂₁ of the final polymer, g/10 min	51	22	20
Density of the final polymer, kg/m ³	922	923	931
Split, loop/gpr	45/55	41/59	41/59

ND denotes that the respective property has not been determined

Example 6

- 5 The procedure of Example 5 was repeated, except that the polymer composition comprised of 40 % by weight of polymer produced in Example 2 as the bimodal polyethylene composition and 60 % by weight of CaCO₃. The composition was then blown to a film and the resulting film was stretched in the machine direction 6 times its original length. The resulting film had a thickness of 19 μm , a basis weight of 16 g/m², tensile strength in the
- 10 machine direction of 59 MPa, and in the transverse direction of 4.1 MPa. Tear strength in

the machine and transverse directions were 1.1 and 43 N, respectively. The water vapour transmission rate was found to be 6280 g/m²/24 h. The film had no pinholes.

Example 7

5 The procedure of Example 5 was repeated, except that the polymer composition comprised of 45 % by weight of polymer produced in Example 3 as the bimodal polyethylene composition and 55 % by weight of CaCO₃. The composition was then blown to a film and the resulting film was stretched in the machine direction 6 times its original length. The resulting film had a thickness of 25 μm, tensile strength in the machine direction of 67
10 MPa, and in the transverse direction of 4.1 MPa. Tear strength in the machine and transverse directions were 1.2 and 47 N, respectively.

Example 8

The procedure of Example 5 was repeated, except that the polymer composition comprised
15 of 45 % of polymer produced in Example 4 as the bimodal polyethylene composition and 55 % of CaCO₃. The composition was then blown to a film and the resulting film was stretched in the machine direction 5 times its original length. The resulting film had a thickness of 28 μm, a basis weight of 26 g/m², tensile strength in the machine direction of 86 MPa, and in the transverse direction of 6.0 MPa. Tear strength in the machine and
20 transverse directions were 1.9 and 112 N, respectively. The water vapour transmission rate was found to be 1930 g/m²/24 h. The film had no pinholes.

Example 9

The procedure of Example 5 was repeated, except that the polymer composition comprised
25 of 25 % of polymer produced in Example 4 as the bimodal polyethylene composition, 20 % of CB9270 (a bimodal linear low density polyethylene designed for extrusion coating, produced and marketed by Borealis, having a density of 927 kg/m³ and MFR₂ of 10 g/10 min), and 55 % of CaCO₃. The composition was then blown to a film and the resulting film was stretched in the machine direction 5 times its original length. The resulting film had a
30 thickness of 21 μm, a basis weight of 23 g/m², tensile strength in the machine direction of 72 MPa, and in the transverse direction of 6.2 MPa. Tear strength in the machine and transverse directions were 1.5 and 100 N, respectively. The water vapour transmission rate was found to be 1090 g/m²/24 h. The film had no pinholes.

Example 10

The procedure of Example 9 was repeated, except that film was stretched in the machine direction 5.5 times its original length. The resulting film had a thickness of 21 μm tensile strength in the machine direction of 85 MPa, and in the transverse direction of 5.5 MPa.

- 5 Tear strength in the machine and transverse directions were 1.2 and 100 N, respectively.

Table 2: Film data of Examples 5 to 10.

Example	5	6	7	8	9	10
CaCO ₃ , wt-%	55	60	55	55	55	55
Olefin polymer, type	SA233FF PP	-	-	-	CB9270 PE	CB9270 PE
Olefin polymer, wt-%	10	0	0	0	20	20
Bimodal composition, wt-%	35	40	45	45	25	25
Stretch ratio	4.7	6.0	6.0	5.0	5.0	5.5
Tensile strength MD, MPa	50	59	67	86	72	85
Tensile strength TD, MPa	5.0	4.1	4.1	6.0	6.2	5.5
Tear strength MD, N	1.2	1.1	1.2	1.9	1.5	1.2
Tear strength TD, N	40	43	47	112	100	100
WVTR, g/m ² /24h	4990	6280		1930	1090	

Claims

- 5 1. A composition for making breathable films, the composition comprising:
(i) 20 – 50 %, based on the weight of the total composition, a bimodal polyethylene composition, further comprising
- 10 (i-a) a first low molecular weight component, which is a homopolymer of ethylene or a copolymer of ethylene and one or more C₄ to C₁₀ alpha-olefins, having a melt flow rate MFR₂ of 50 to 500 g/10 min, preferably of 100 to 400 g/10 min and a density of 940 to 975 kg/m³, preferably 945 to 975 kg/m³, the first component being present in the bimodal polyethylene composition in an amount of 37 to 48 % by weight,
- 15 (i-b) at least a second component, which is a copolymer of ethylene and one or more C₄ to C₁₀ alpha-olefins, having a higher molecular weight, a lower melt index and a lower density than the said first component, the second component being present in the bimodal polyethylene composition in an amount of 52 to 63 % by weight, so that the said bimodal polyethylene composition has a melt flow rate MFR₂ in the range of 0.1 to 4.0 g/10 min, preferably 0.1 to 0.8 g/10 min, MFR₂₁ in the range of 15 to 200 g/10 min, preferably 15 to 70 g/10 min and a density of 918 to 935 kg/m³,
- 20 (ii) 40 – 70 %, based on the weight of the total composition, a particulate filler, and
(iii) 0 – 30 %, based on the weight of the total composition, another olefin-based polymer.
- 25 2. The composition according to Claim 1, wherein the other olefin based polymer is selected from the group of homo- and copolymers propylene, 1-butene and 4-methyl-1-pentene.
- 30 3. The composition according to Claim 1 or 2, wherein the other olefin based polymer is a propylene homo- or copolymer, preferably a copolymer of propylene and ethylene.
4. The composition according to Claim 3, wherein the composition comprises of 5 to 20 %, based on the weight of the total composition, of the said propylene polymer.

5. The composition according to Claim 1, wherein the content of the particulate filler is 55 to 70 %.

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6. A composition according to any one of the preceding claims, wherein the particulate filler is calcium carbonate.

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7. A composition for making breathable films, the composition comprising:

(i) 20 – 50 %, based on the weight of the total composition, a bimodal polyethylene composition having the following properties (a) to (d):

(a) density from 912 to 935 kg/m³;

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(b) melt index MFR₂ from 0.1 to 0.8 g/10 min;

(c) melt index MFR₂₁ from 15 to 70 g/10 min;

(d) flow rate ratio MFR₂₁/MFR₂ from 60 to 120,

(ii) 40 – 70 %, based on the weight of the total composition, a particulate filler, and

(iii) 0 – 30 %, based on the weight of the total composition, another olefin-based polymer.

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8. A composition according to Claim 7, wherein the bimodal polyethylene composition has:

(e) a weight average molecular weight (M_w) from 150000 to 300000 g/mol;

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(f) a ratio of the weight average molecular weight to the number average molecular weight (M_w/M_n) from 7 to 30; and

(g) a content of alpha-olefin comonomer units of 2 to 5 % by mole.

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9. The composition according to any one of Claims 7 or 8, wherein the other olefin based polymer is a propylene homo- or copolymer, preferably a copolymer of propylene and ethylene.

10. The composition according to Claim 9, wherein the composition comprises of 5 to 20 %, based on the weight of the total composition, of the said propylene polymer.
- 5 11. The composition according to any one of Claims 7 or 8, wherein the content of the particulate filler is 55 to 70 %.
12. A composition according to any one of Claims 7 to 11, wherein the particulate filler is
10 calcium carbonate.
13. The use of the composition according to any one of Claims 1 to 12 for making films.
- 15 14. A breathable polymer film, which film comprises a composition according to any one of Claims 1 to 12.
- 20 15. A film according to Claim 14 wherein the film has a water vapour transmission rate of more than 3000 g/m²/24 h, preferably more than 4000 g/m²/24 h.
16. A film according to any one of Claims 14 to 15, wherein the film has a basis weight of
25 less than 25 g/m².
17. A process for producing a breathable polymer film, comprising the steps of:
(A) providing into an extruder a composition according to any one of Claims 1 to 12
30 (B) extruding the composition to a film
(C) stretching the film to produce a breathable film.

18. The process according to Claim 17, wherein the film is stretched with a stretching ratio of 3 to 10, preferably 4 to 7.

5 19. The process according to any one of Claims 17 to 18, wherein the bimodal polyethylene composition has been produced by a process comprising the steps of:

- (i) 10 subjecting ethylene, hydrogen and optionally comonomers to a first polymerisation or copolymerisation reaction in the presence of the polymerisation catalyst in a first reaction zone or reactor to produce a first polymerisation product having a low molecular weight with a melt flow rate MFR_2 of 50 to 500 g/10 min, preferably of 100 to 400 g/10 min and a density of 940 to 975 kg/m³, preferably 945 to 975 kg/m³,
- (ii) recovering the first polymerisation product from the first reaction zone,
- (iii) feeding the first polymerisation product into a second reaction zone or reactor,
- 15 (iv) feeding additional ethylene, comonomers and optionally hydrogen to the second reaction zone,
- (v) subjecting additional ethylene and additional comonomer(s) and optionally hydrogen to the second reaction zone in the presence of the said polymerisation catalyst and the first polymerisation product,
- 20 (vi) to produce a polymer composition comprising from 41 to 48 % by weight of the low molecular weight polymer produced in step (i), and from 59 to 52 % by weight of the high molecular weight component produced in step (v),
- (vii) the composition having a melt flow rate in the range MFR_2 of 0.1 to 4.0 g/10 min, preferably 0.1 to 0.8 g/10 min and a density of 918 to 935 kg/m³, and
- 25 (viii) recovering the combined polymerisation product from the second reaction zone.

20. The process according to Claim 19, wherein at least part of the volatile components of the reaction medium are evaporated and removed from the first polymerisation product before the said first polymerisation product is introduced into the second reaction zone or
30 reactor.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/FI 03/00501

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08L23/06 C08J5/18 C08F2/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08L C08J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6 096 014 A (HAFFNER WILLIAM B ET AL) 1 August 2000 (2000-08-01) examples B, G	1-20
Y	WO 99 41310 A (BOREALIS POLYMERS OY ; NUMMILA PAKARINEN AULI (FI); MYHRE OLE JAN () 19 August 1999 (1999-08-19) example 1	1-20
A	US 5 405 901 A (TILSTON MICHAEL W ET AL) 11 April 1995 (1995-04-11) example 1	1-20

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 6096014	A	01-08-2000	AU 733555 B2	17-05-2001
			AU 5804798 A	31-07-1998
			BR 9714089 A	13-11-2001
			CN 1258305 A	28-06-2000
			EP 0948558 A1	13-10-1999
			WO 9829481 A1	09-07-1998
<hr/>				
WO 9941310	A	19-08-1999	AU 741744 B2	06-12-2001
			AU 2425999 A	30-08-1999
			BR 9907836 A	24-10-2000
			CA 2320295 A1	19-08-1999
			CN 1296511 T	23-05-2001
			EP 1054927 A1	29-11-2000
			WO 9941310 A1	19-08-1999
			JP 2002503743 T	05-02-2002
			US 6552150 B1	22-04-2003
			ZA 9901048 A	11-08-1999
<hr/>				
US 5405901	A	11-04-1995	AU 678658 B2	05-06-1997
			AU 1148495 A	18-01-1996
			BR 9500391 A	18-06-1996
			CA 2141474 A1	07-01-1996
			EP 0691353 A1	10-01-1996
			JP 8027205 A	30-01-1996
<hr/>				

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